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The Optical Properties of Uranium Carbide and its Rate of Oxidation in Air Determined by Spectroscopic Ellipsometry

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The optical properties of uranium carbide and its rate of oxidation in air determined by spectroscopic ellipsometry.

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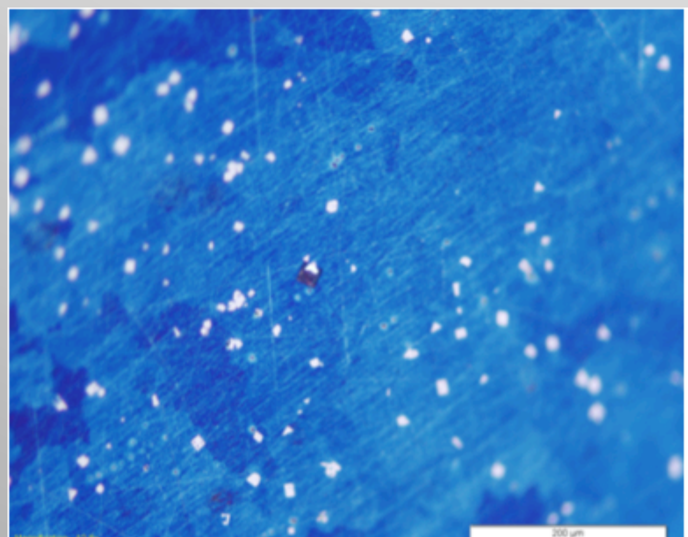
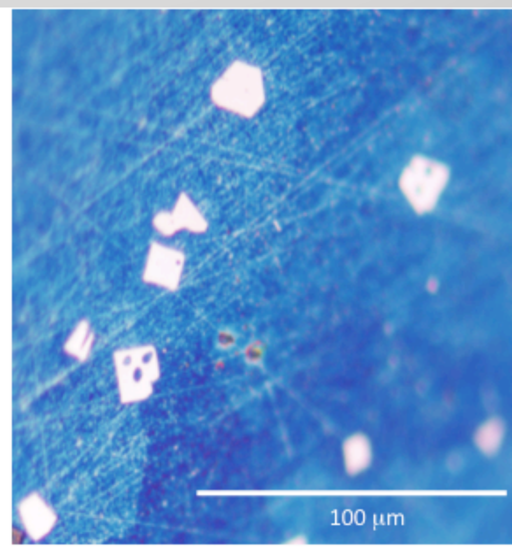
Motivation

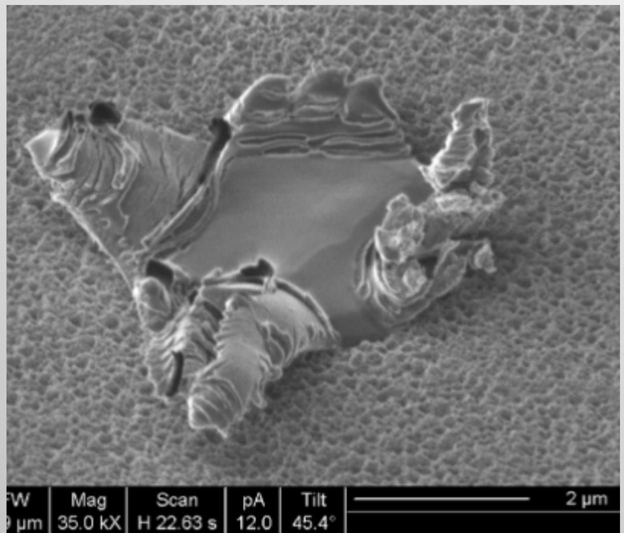
- Uranium carbide is used
  - as fuel in fast breeder reactors
  - as fuel (UC_2) in high temperature gas cooled reactors
- Uranium carbide
  - Appears as inclusions in uranium metal
  - Up to 300 weight ppm, 0.009 volume fraction





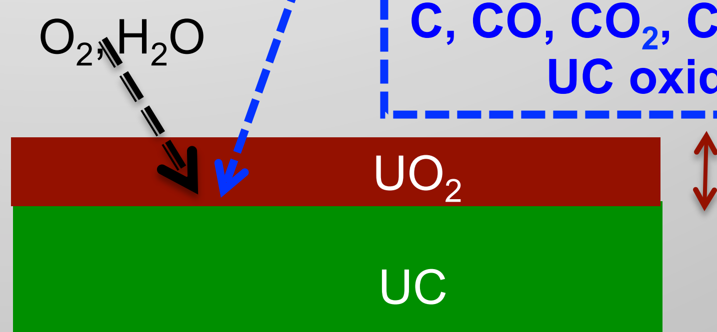
Uranium Carbide Oxidation

- $UC(s) + 2H_2O(g) \rightarrow UO_2(s) + C(s) + 2H_2(g)$ (1)
  $UC(s) + 2H_2O(g) \rightarrow UO_2(s) + CH_4(g)$ (2)



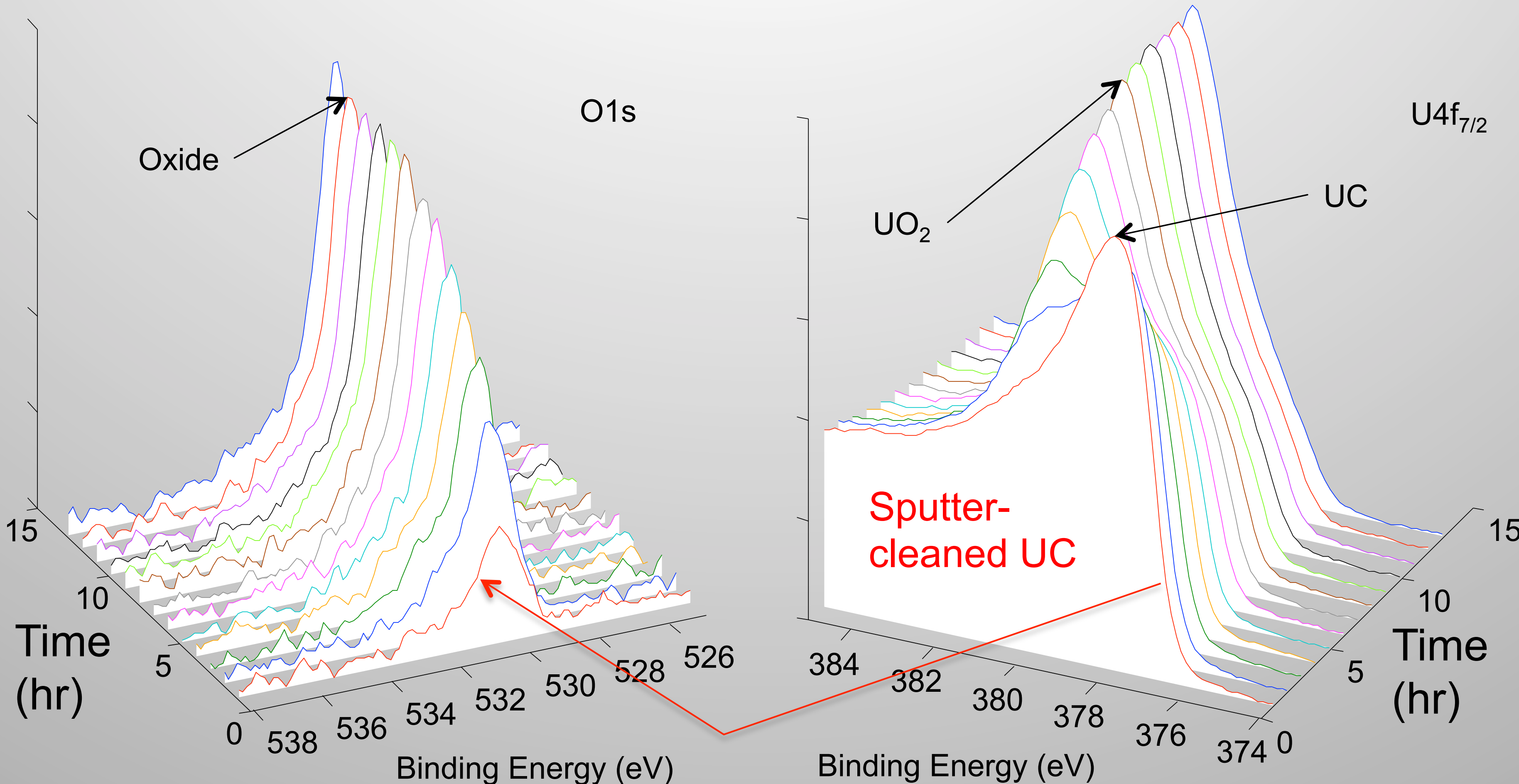
24 h at 20 mbar water vapour pressure **(NO O_2)** and 20° C. T.B. Scott et al. / Journal of Hazardous Materials *195 (2011) 115–123*

Oxidation occurs at the UC/UO_2 interface. **Where does C, CO, CO_2, CH_4 go during UC oxidation?**

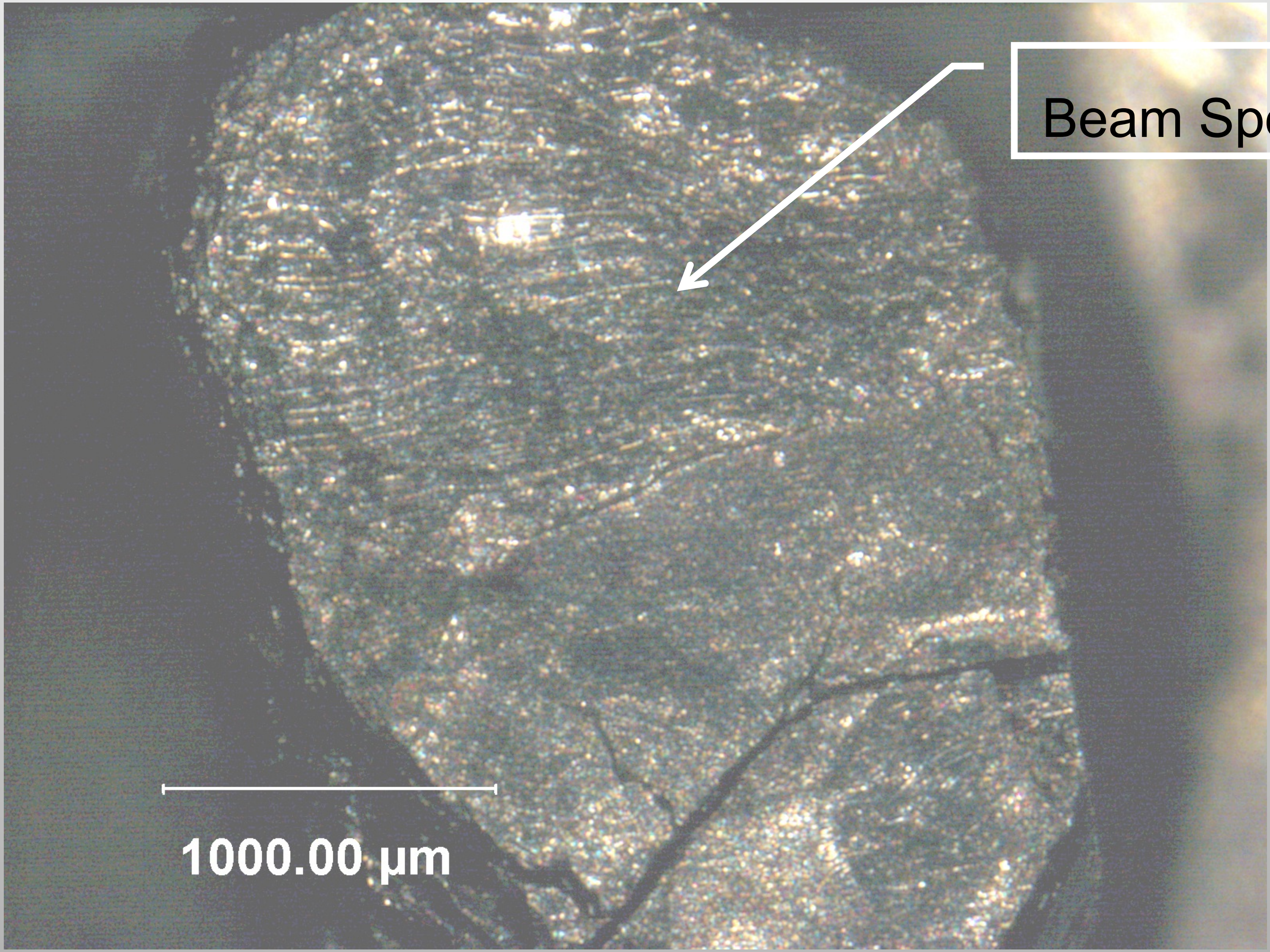


- $UC(s) + 2O_2(g) \rightarrow UO_2(s) + CO_2(g)$ (3)
  $2UC(s) + 3O_2(g) \rightarrow 2UO_2(s) + 2CO(g)$ (4)

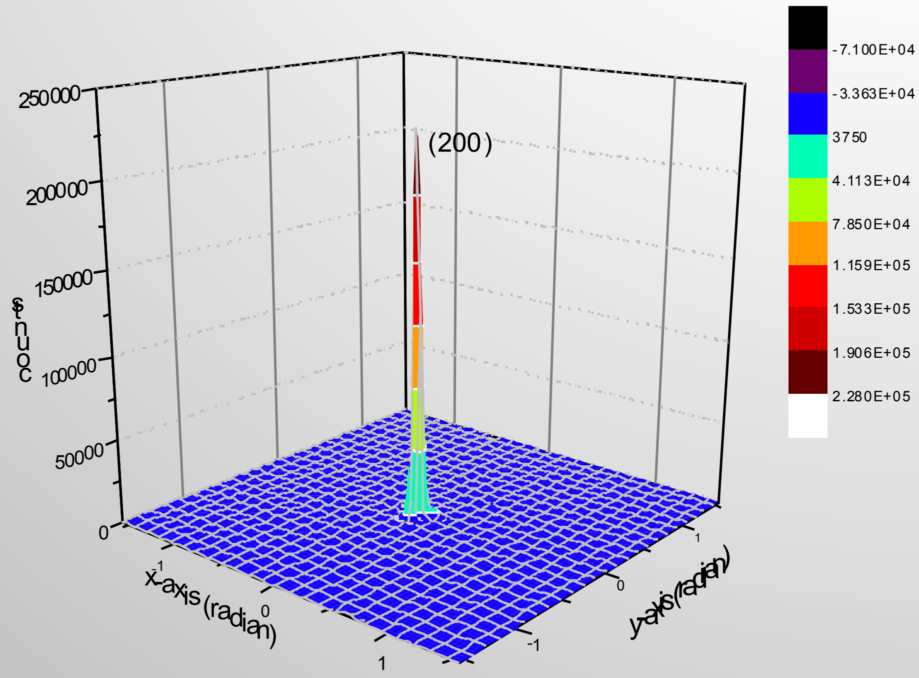
UC Oxidation in UHV: XPS of O and U



Sputter-cleaned UC crystal



X-ray diffraction of UC single crystal



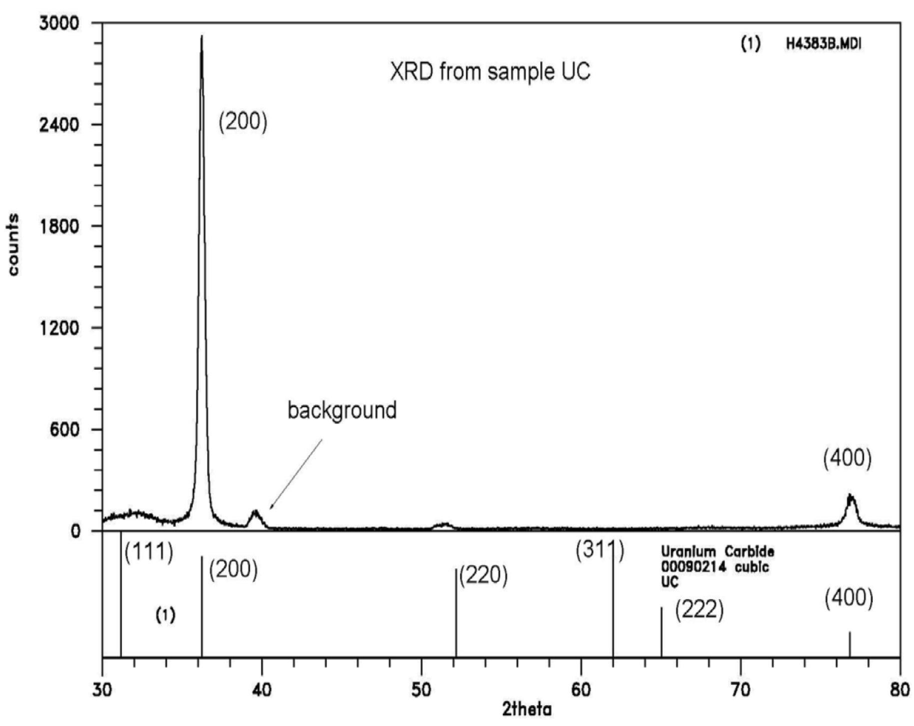
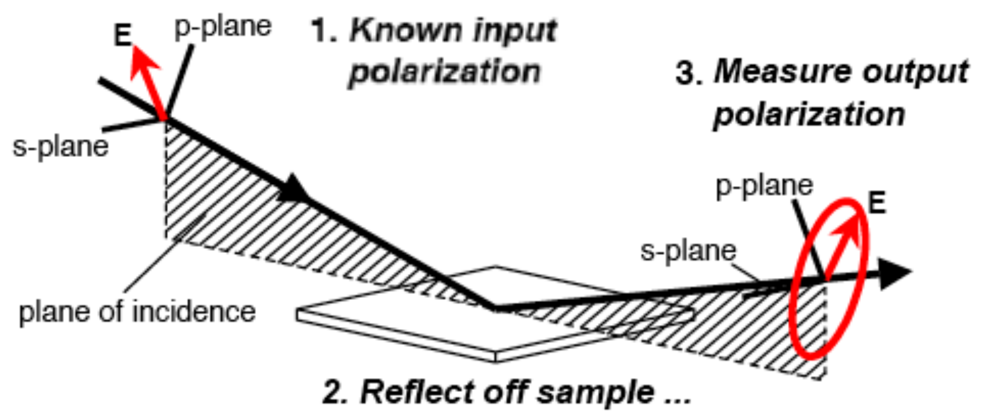


Figure 1: XRD diffraction pattern for sample (a)

By scanning χ and ϕ, a two dimensional map of the (200) peak is acquired that indicates that

[100] planes are parallel to the sample's surface

Ellipsometric spectroscopy measures the complex reflection coefficient ρ as f(photon energy).



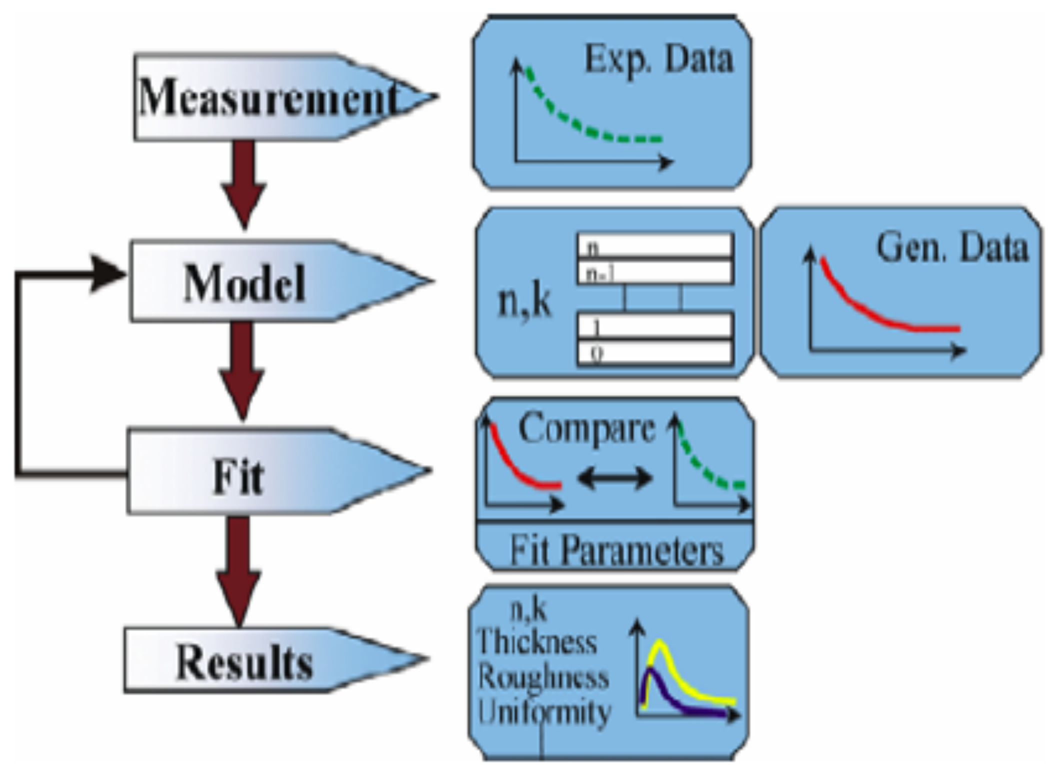
$$\rho = \frac{R_P}{R_S} = \tan(\psi)e^{i\Delta}$$

R_{p}, R_s are the complex Fresnel reflection coefficients

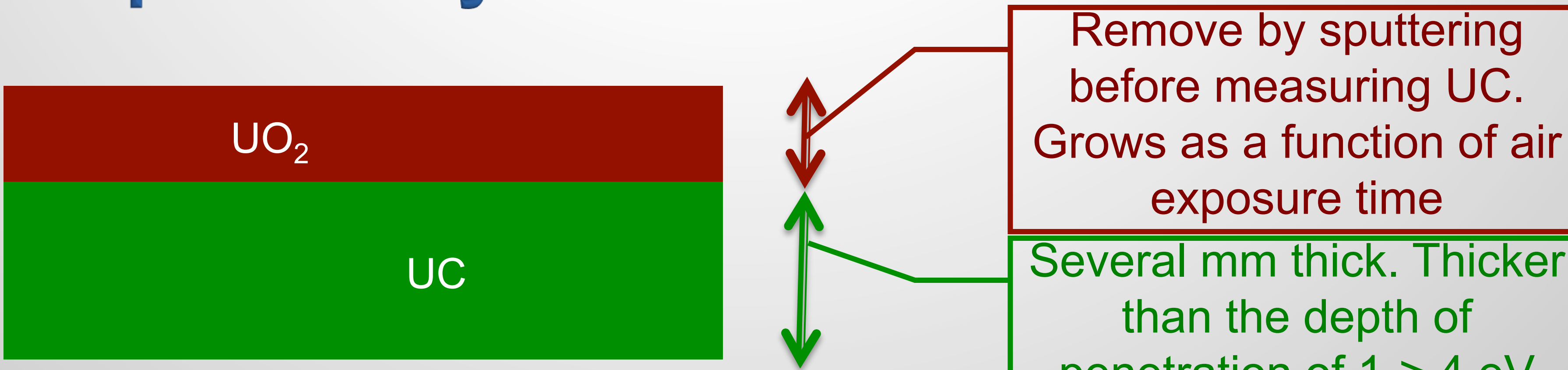
- **Ellipsometry:** measures Δ and Ψ with 1mm Ø beam as a function of photon energy at several angles of incidence
- **Constants ($n,k,\varepsilon_1,\varepsilon_2$):** are derived by **fitting** optical materials models (Cauchy, Urbach, Oscillator ..model)
- **Quality of fit** is determined by calculating the mean square error (MSE) value.

$$MSE = \sqrt{\frac{1}{2N-M}\sum_{n=1}^{N}\left[\left(\frac{\Psi_i^{mod}-\Psi_i^{exp}}{\sigma_{\Psi,i}^{exp}}\right)^2+\left(\frac{\Delta_i^{mod}-\Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}}\right)^2\right]}$$

M = Number of fit parameter



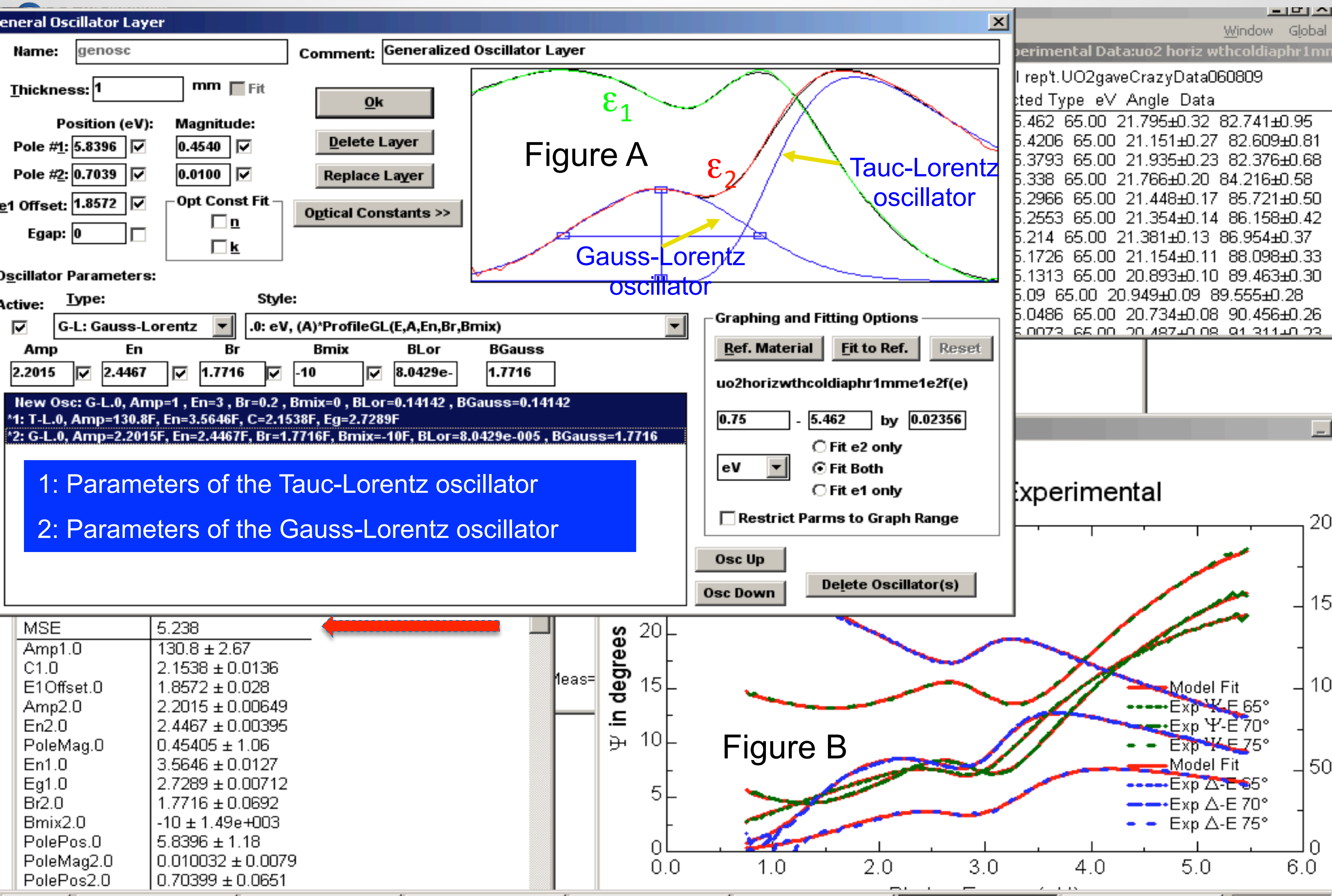
Ellipsometry Work Outline



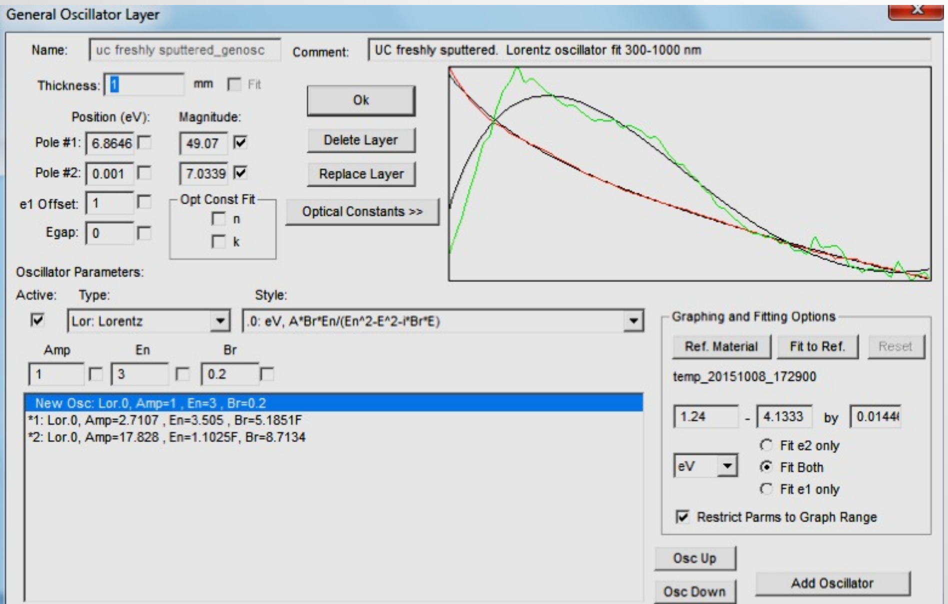
- Measure Δ,Ψ of a UO_2 crystal
  - Create optical model of UO_2 and a file of n,k (or ε_1, ε_2)
- Measure UC's Δ and Ψ after sputter-removing UO_2
  - Create optical model of UC and a file of n,k (or ε_1, ε_2)
- Measure Δ and Ψ changes as UO_2 grows on UC
  - Determine the thickness of UO_2 that minimizes MSE

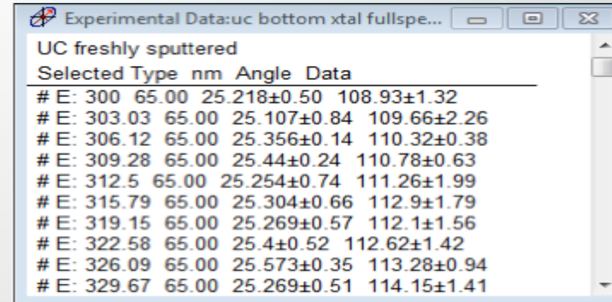
<111> UO_2: Δ ,Ψ & optical model

Siekhaus,Crowhurst OP Conf. Series:
Mat. Sci. and Eng.**9** (2010) 012055
doi:10.1088/1757-899X/9/1/012055



Sputtered UC: Δ ,Ψ, & optical model

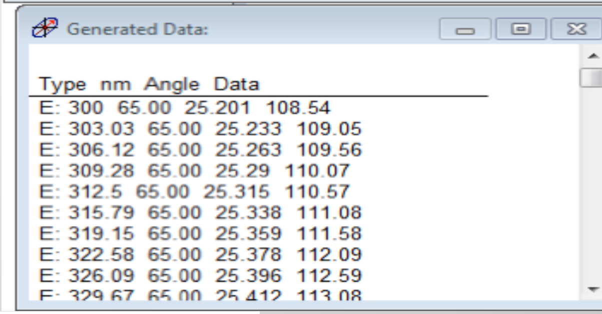




Experimental Data:uc bottom xtal fullspe...

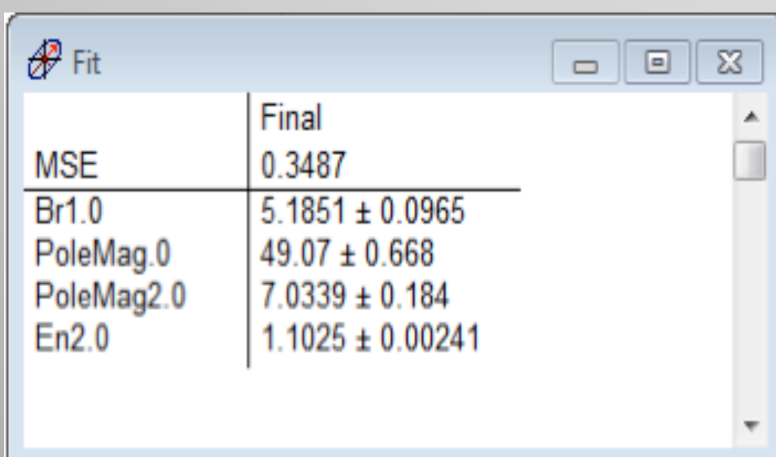
UC freshly sputtered

Selected	Type	nm	Angle	Data	
#	E:	300	65.00	25.218±0.50	108.93±1.32
#	E:	303.03	65.00	25.107±0.84	109.66±2.26
#	E:	306.12	65.00	25.356±0.14	110.32±0.38
#	E:	309.28	65.00	25.44±0.24	110.78±0.63
#	E:	312.5	65.00	25.254±0.74	111.26±1.99
#	E:	315.79	65.00	25.304±0.66	112.9±1.79
#	E:	319.15	65.00	25.269±0.57	112.1±1.56
#	E:	322.58	65.00	25.4±0.52	112.62±1.42
#	E:	326.09	65.00	25.573±0.35	113.28±0.94
#	E:	329.67	65.00	25.269±0.51	114.15±1.41



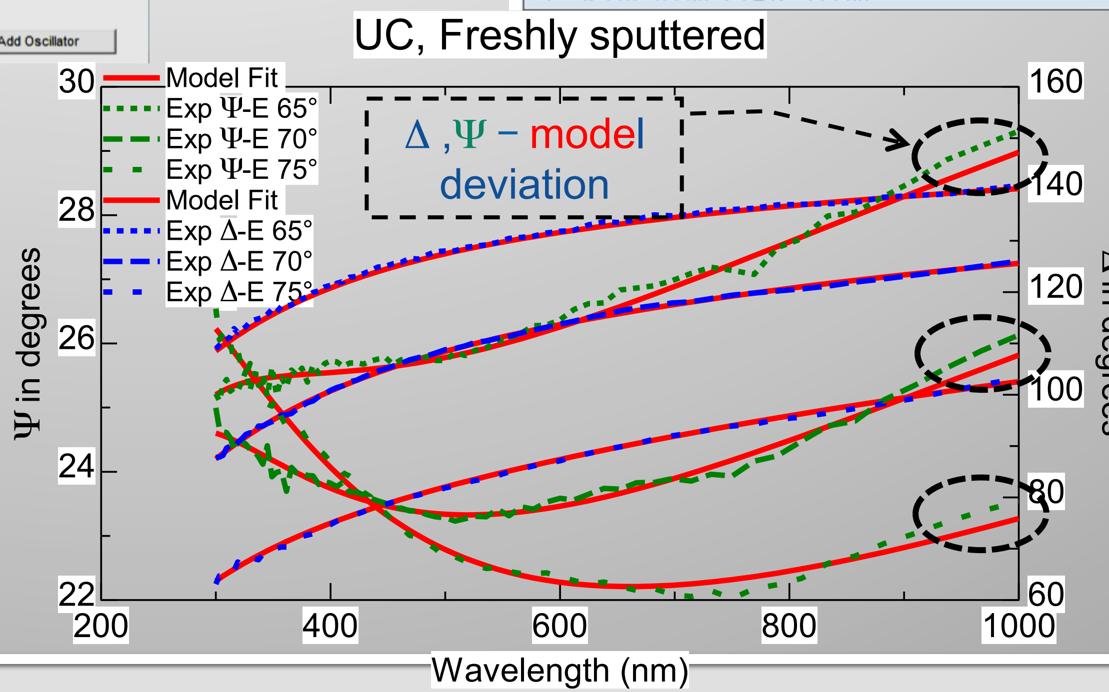
Generated Data:

Type	nm	Angle	Data	
E:	300	65.00	25.201	108.54
E:	303.03	65.00	25.233	109.05
E:	306.12	65.00	25.263	109.56
E:	309.28	65.00	25.29	110.07
E:	312.5	65.00	25.315	110.57
E:	315.79	65.00	25.338	111.08
E:	319.15	65.00	25.359	111.58
E:	322.58	65.00	25.378	112.09
E:	326.09	65.00	25.396	112.59
E:	329.67	65.00	25.412	113.08

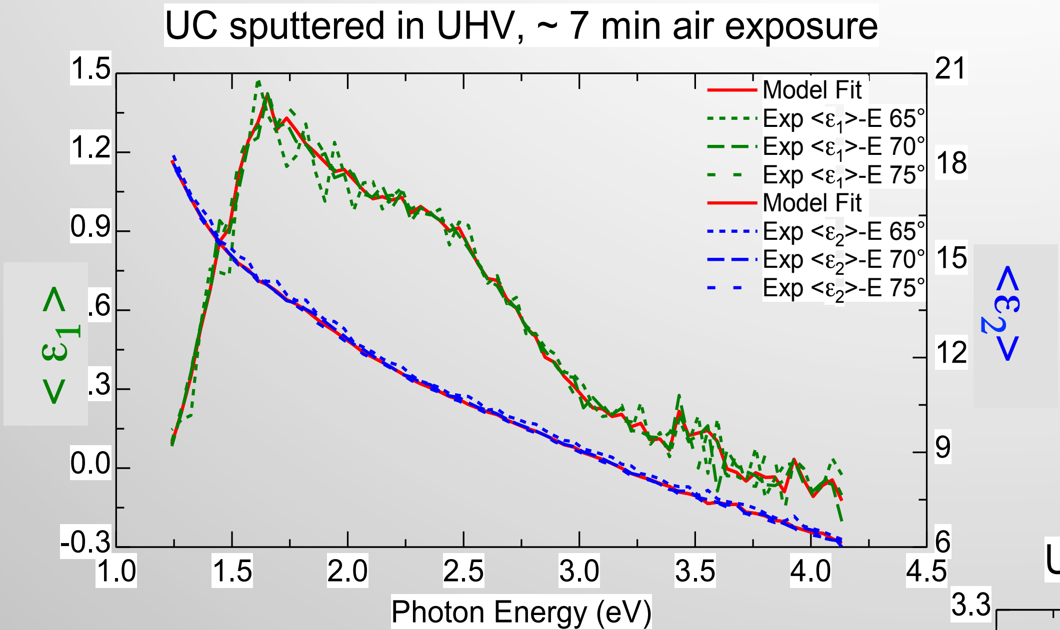


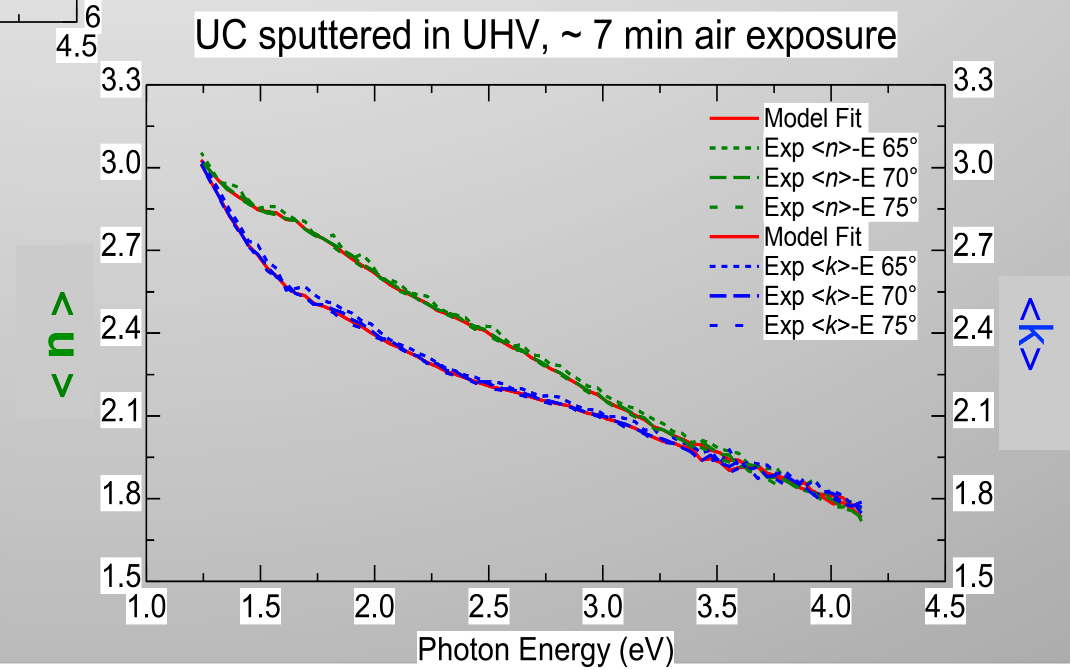
Fit

	Final
MSE	0.3487
Br1.0	5.1851 ± 0.0965
PoleMag.0	49.07 ± 0.668
PoleMag2.0	7.0339 ± 0.184
En2.0	1.1025 ± 0.00241



UC's optical constants ε_1, ε_2 & n, k.





Ellipsometry of UO_2 growth on UC

Ellipsometry Material files

1 uo2 horiz wthcoldiaphr1mm_g1(nc 0.514 nm anl uo2

0 uc freshly sputtered_genosc f(energy 1 mm

Growing UO_2 changes Δ and Ψ

Thickness grows as a function of exposure time to air

UC, contribution to Δ and Ψ is fixed

Fixed thickness and ellipsometry material model

- Measure Δ and Ψ as UO2 grows on UC
  - "Fit" the thickness of UO_2 that minimizes UO_2 MSE

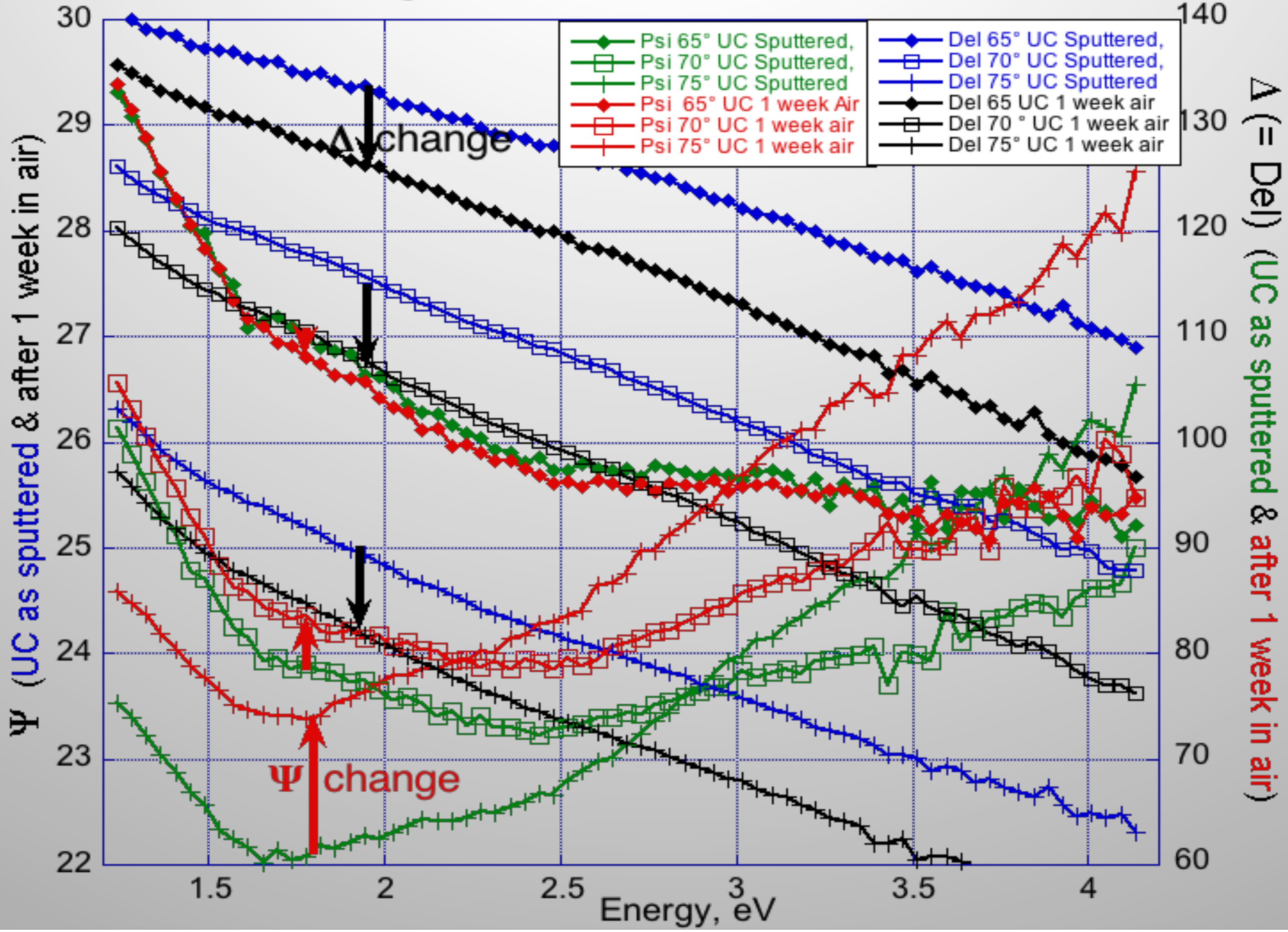
Fit

	Final
MSE	0.5867
Thick 1	0.514 ± 0.0247

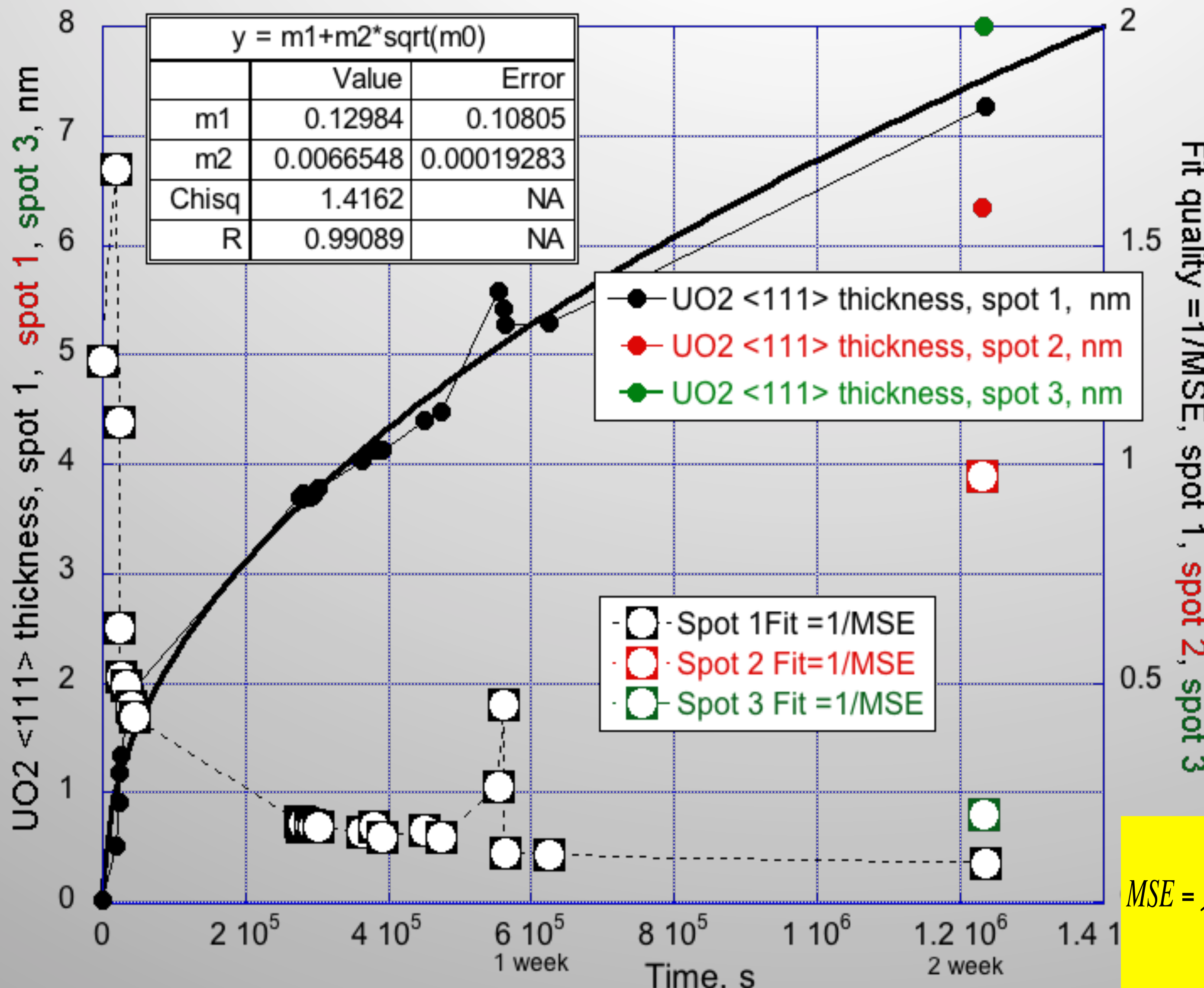
$$MSE = \sqrt{\frac{1}{2N-M}\sum_{n=1}^{N}\left[\left(\frac{\Psi_i^{mod}-\Psi_i^{exp}}{\sigma_{\Psi,i}^{exp}}\right)^2+\left(\frac{\Delta_i^{mod}-\Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}}\right)^2\right]}$$

M = Number of fit parameter

Δ and Ψ change due to 1 week air exposure



Oxide growth (~√time) on UC in air & fit quality

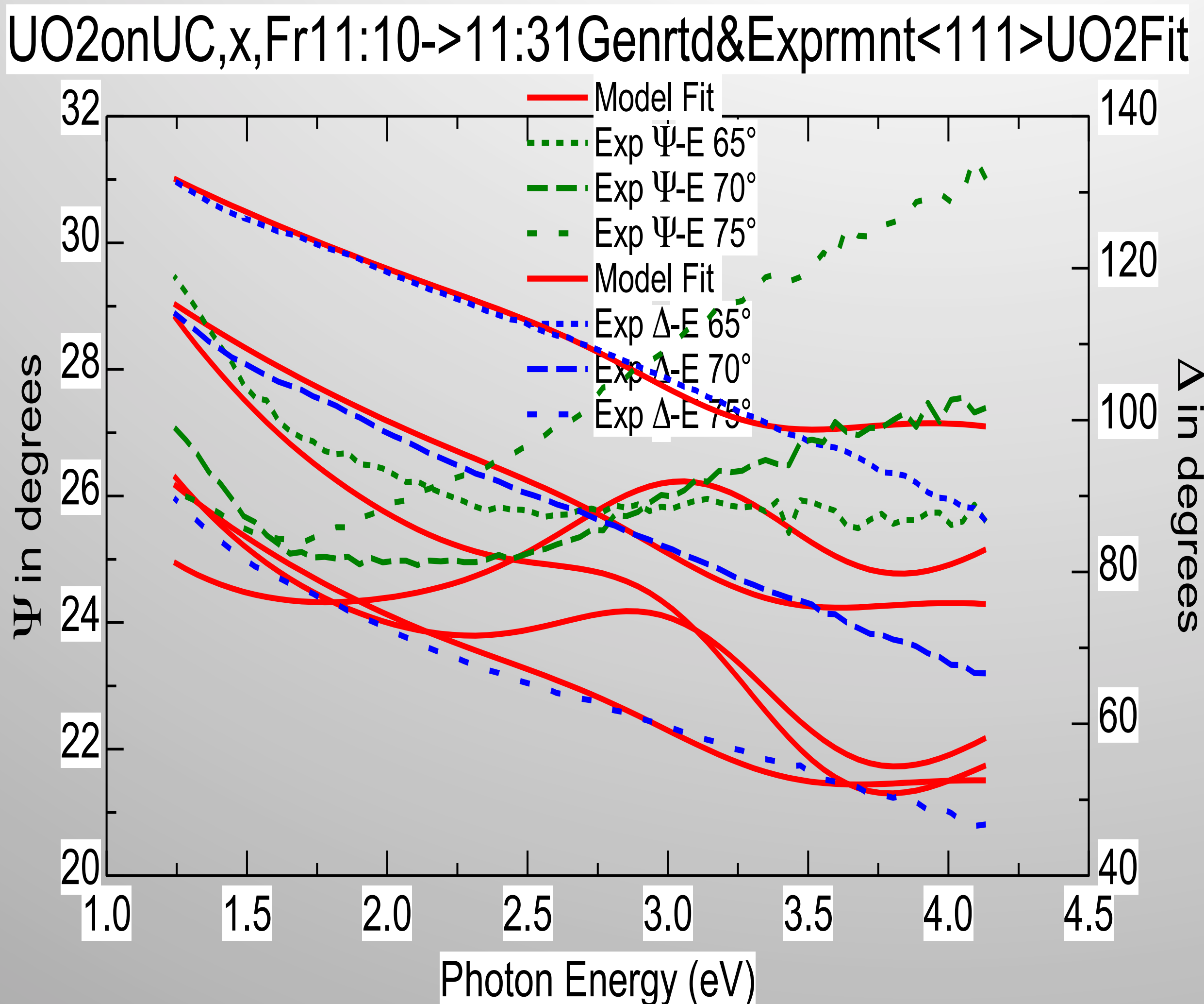


- The "Fit quality" = 1/MSE decreases with increasing UO2 thickness
  - >>The "oxide" is NOT pure UO_2

$$MSE = \sqrt{\frac{1}{2N-M}\sum_{n=1}^{N}\left[\left(\frac{\Psi_i^{mod}-\Psi_i^{exp}}{\sigma_{\Psi,i}^{exp}}\right)^2+\left(\frac{\Delta_i^{mod}-\Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}}\right)^2\right]}$$

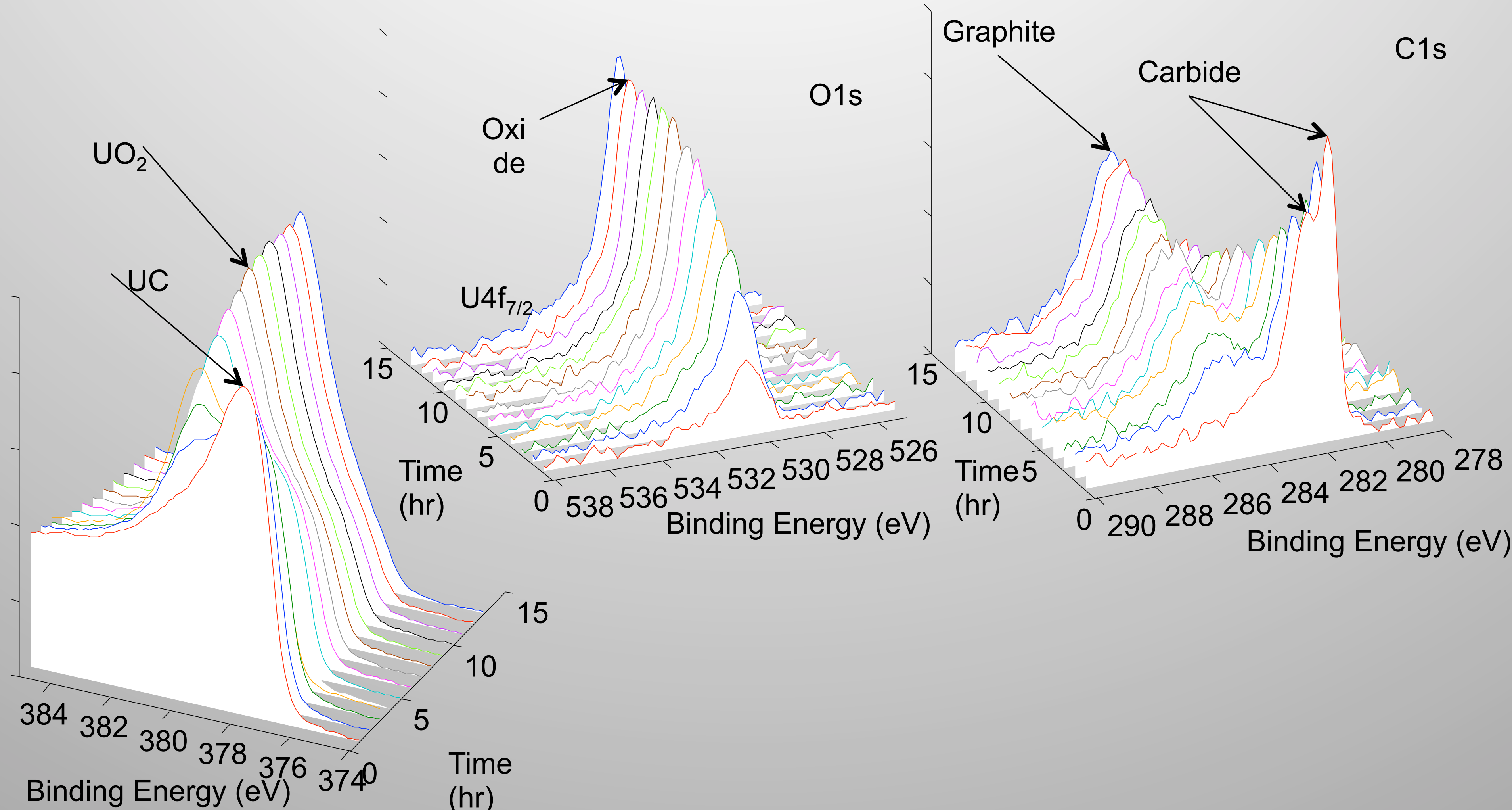
M = Number of fit parameter

Model Fit and experimental Δ and Ψ *at Final* Spot 1 (~ 7 nm UO_2)



- Good fit to Δ below 3.5 eV
- Bad fit to Ψ
  - Particularly the 'upward' movement of Ψ at 75° is completely missing
- >>The "oxide" is NOT pure UO_2

XPS: A graphitic carbon peak grows in/on the oxide of UC as it oxidizes in UHV



1) The optical properties of uranium carbide 2) its rate of oxidation in air determined by spectroscopic ellipsometry.

- 1)The optical constants (ε_1, ε_2) and (n, k) of a sputter-cleaned surface of single crystal UC have been determined by spectroscopic ellipsometry.
- 2) Changes in Δ and Ψ during exposure to air of UC were measured as a function time.
- 2) A growth curve (~ √time) of oxide on UC was developed using an optical materials file of UO_2 to fit those changes in Δ and Ψ.
  - The quality of fit decreased with increasing oxide thickness, indicating that the oxide is most likely NOT pure UO_2
  - The 'fate' of carbon during oxidation is a possible reason.
    - XPS sees only the surface.
    - SIMS depth profiling will determine C distribution throughout the layer

Woollam company helped to develop oscillator models for UO_2 and UC.

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